



Short communication

## Spinel $ZnCo_2O_4$ /N-doped carbon nanotube composite: A high active oxygen reduction reaction electrocatalyst



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### HIGHLIGHTS

- We demonstrate the first solvothermal preparation of  $ZnCo_2O_4$ /NCNT composite.
- The composite exhibits high ORR performance in alkaline solution.
- The composite has superior methanol tolerance ability and durability to Pt/C catalyst.

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### ABSTRACT

In this communication, we report on the solvothermal preparation of spinel  $ZnCo_2O_4$ /N-doped carbon nanotube ( $ZnCo_2O_4$ /NCNT) composite. As a novel oxygen reduction reaction (ORR) electrocatalyst, the  $ZnCo_2O_4$ /NCNT composite shows high activity via a four-electron pathway in alkaline solution. Such catalyst also exhibits superior methanol tolerance ability and durability over commercial Pt/C catalyst.

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### 1. Introduction

Fuel cells are attractive clean energy technology with low or zero emissions from operation. However, the sluggish kinetics of cathodic oxygen reduction reaction (ORR) significantly limits the efficiency and performance of electrochemical energy conversion [1]. Thus, a highly active catalyst for four-electron ORR is essential to improve the reaction rate and lower the reaction overpotential. So far, precious Pt and its alloys have been considered to be the most reliable ORR electrocatalysts [2,3]; however, its high cost, resource scarcity, and weak durability hinder its large-scale

commercial production and application [4–6]. As such, extensive efforts have been devoted to developing low-cost alternatives such as non-precious metals [7], non-precious metal oxides [8], carbon-based materials doped with heteroatoms [9], or carbon-supported transition metal-nitrogen complexes [10], etc.

Mixed valence oxides of transition metals with a spinel structure are important class of metal oxides that exhibit excellent ORR catalytic activity and cobalt based spinel oxides have been extensively investigated as ORR catalyst due to its high activity, low cost, and high stability [11]. The use of carbon support can further increase the dispersion and utilization of the active catalyst, thereby improving its catalytic activity. On the other hand, N-incorporation into the carbon matrix can increase its ORR activity [12]. Indeed, much attention has been paid to develop metal oxide/N-doped carbon composite toward ORR or electrochemical energy storage applications [13]. However, to the best of our knowledge, the preparation of spinel  $ZnCo_2O_4$  and N-doped carbon nanotube

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(ZnCo<sub>2</sub>O<sub>4</sub>/NCNT) composite ORR catalyst has never been addressed before. In this communication, we demonstrate the first preparation of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT composite via a solvothermal strategy. We further demonstrate that, although ZnCo<sub>2</sub>O<sub>4</sub> or NCNT alone has low ORR activity, such composite exhibits high ORR performance in alkaline solution via a four-electron pathway. It also suggests that this catalyst shows superior methanol tolerance ability and durability to commercial Pt/C catalyst.

## 2. Experimental

### 2.1. Reagents and materials

Multiwall CNTs, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma–Aldrich. Concentrated hydrochloric acid and KMnO<sub>4</sub> were purchased from Beijing Chemical Corp. Ammonia (25 wt%) and anhydrous ethanol (EtOH) were purchased from Tianjin Fuyu Fine Chemical Research Institute. Co(OAc)<sub>2</sub>·6H<sub>2</sub>O was purchased from Tianjin Fuchen Chemical Reagent Factory. Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was purchased from Xilong Chemical Co., Ltd. All the chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

### 2.2. Oxidative treatment of CNTs

To obtain water-soluble CNTs, the pristine CNTs were subjected to oxidative treatment according to reported method [14]. Briefly, 60 mg of CNTs was suspended in 50 mL of a 3:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> and sonicated in a water bath for 24 h (ultrasonication power of 60 W). The resulting products were collected by centrifugation and washed with water for three times, then dried at 80 °C overnight.

### 2.3. Preparation of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT composite

In a typical synthesis, 0.72 mmol Co(OAc)<sub>2</sub>·6H<sub>2</sub>O, 0.36 mmol Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 36 mg CNTs were dispersed in 48 mL of EtOH, followed by addition of 1 mL ammonia at room temperature. The reaction was kept at 80 °C with stirring for 10 h. After that, the reaction mixture was transferred to a 40 mL-Teflon-lined autoclave, and then the autoclave was placed in an oven at 150 °C for 10 h. The resulting products were collected by centrifugation and washed with pure ethanol for three times, then dried at 80 °C overnight.

ZnCo<sub>2</sub>O<sub>4</sub>, NCNT, and Co<sub>3</sub>O<sub>4</sub>/NCNT composite were made using the same method. The ZnCo<sub>2</sub>O<sub>4</sub> and NCNT physical mixture was obtained by sonicating ZnCo<sub>2</sub>O<sub>4</sub> and NCNT mixture with a mass ratio of 1:1.

### 2.4. Characterizations

Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscope (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) experiments were made on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Powder X-ray diffraction (XRD) data were recorded on a RigakuD/MAX 2550 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

### 2.5. Electrode preparation and electrochemical measurements

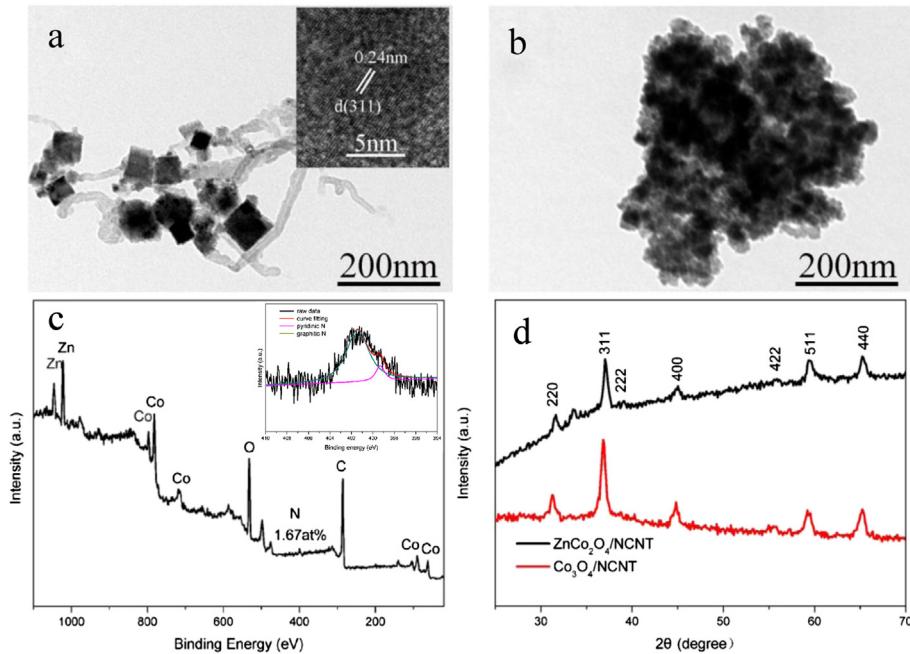
Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out with a conventional three electrode system with N<sub>2</sub> and O<sub>2</sub>-saturated 0.1 M KOH aqueous solution. The

Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. Glassy carbon electrode (GCE, diameter = 5 mm, Pine Instruments) was used as the working electrode. 4 mg catalyst and 10  $\mu\text{l}$  5 wt% Nafion solution were dispersed in 1 mL 1:1 v/v water/ethanol mixed solvent by 30-min sonication to form an ink finally. Then 10- $\mu\text{l}$  catalyst ink was loaded on a GCE with a catalyst loading of 0.04 mg cm<sup>-2</sup>. The CV tests and the LSV measurements were performed at a scan rate of 20 mV s<sup>-1</sup> and 5 mV s<sup>-1</sup>, respectively, in a range from −0.8 V to 0.1 V.

## 3. Results and discussion

Fig. 1a shows the TEM image of the resulting composite, suggesting it consists of CNTs covered with well-separated nanoparticles and nanocubes. The high-resolution TEM (HRTEM) image taken from one nanocube reveals clear lattic fringes with an interplane distance of 0.24 nm corresponding to the (311) plane of spinel ZnCo<sub>2</sub>O<sub>4</sub>. In contrast, the same preparation without the presence of CNTs only leads to nanoparticle aggregates, as shown in Fig. 1b. Such observations indicate that CNTs can effectively increase the dispersion of the catalysts. Fig. 1c shows the XPS survey spectra of the composite, indicating the existence of C, N, O, Zn and Co elements, and the total N content is about 1.67 %. The deconvoluted XPS N 1s spectrum (inset) shows the existence of two types of N chemical states: pyridinic N and graphitic N [15]. Fig. 1d shows the XRD pattern of the composite. For comparative study, the XRD pattern of Co<sub>3</sub>O<sub>4</sub>/NCNT composite is also given. As indicated, the diffraction peaks are well-indexed to the (220), (311), (222), (400), (422), (511) and (440) planes of cubic ZnCo<sub>2</sub>O<sub>4</sub> with a spinel structure (JCPDS no. 23-1390). All these observations indicate the successful preparation of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT composite. Given that cobalt is toxic and expensive [16], it is thus needed to partially replace the Co in Co<sub>3</sub>O<sub>4</sub> with more environment-friendly and earth-abundant metals. Co<sub>3</sub>O<sub>4</sub> takes a cubic spinel structure (space group: Fd3m) with Co<sup>2+</sup> and Co<sup>3+</sup> being located at tetrahedral and octahedral sites, respectively. In this study, partial replacement of Co in Co<sub>3</sub>O<sub>4</sub> with much cheaper and greener Zn leads to isomorphic spinel ZnCo<sub>2</sub>O<sub>4</sub>.

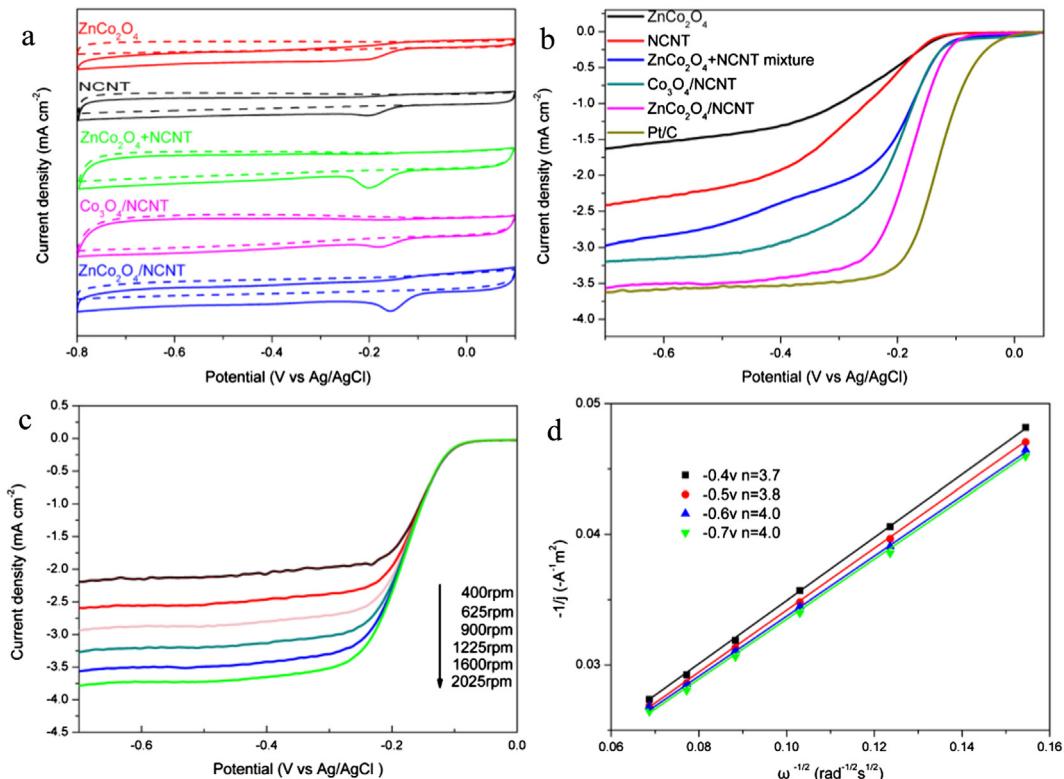
Fig. 2a shows the CV curves of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT, ZnCo<sub>2</sub>O<sub>4</sub>, NCNT, physical mixture of ZnCo<sub>2</sub>O<sub>4</sub> and NCNT (ZnCo<sub>2</sub>O<sub>4</sub>+NCNT), and Co<sub>3</sub>O<sub>4</sub>/NCNT at the same catalyst loading in N<sub>2</sub> and O<sub>2</sub>-saturated 0.1 M KOH solution. In N<sub>2</sub>-saturated solution, all catalysts show no redox peaks in the potential range from −0.8 to 0.1 V. In contrast, distinct peaks corresponding to the ORR are observed for all catalysts in O<sub>2</sub>-saturated solution. Note that ZnCo<sub>2</sub>O<sub>4</sub>/NCNT composite shows a reduction peak at −0.16 V, which is more positive than that of ZnCo<sub>2</sub>O<sub>4</sub> (−0.21 V), NCNT (−0.20 V), ZnCo<sub>2</sub>O<sub>4</sub> + NCNT (−0.19 V), and Co<sub>3</sub>O<sub>4</sub>/NCNT (−0.18 V). Fig. 2b shows the LSVs of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT, ZnCo<sub>2</sub>O<sub>4</sub>, NCNT, ZnCo<sub>2</sub>O<sub>4</sub> + NCNT, Co<sub>3</sub>O<sub>4</sub>/NCNT, and commercial Pt/C in O<sub>2</sub>-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm. ZnCo<sub>2</sub>O<sub>4</sub>/NCNT shows higher diffusion-limiting current density and more positive onset potential than ZnCo<sub>2</sub>O<sub>4</sub>, NCNT, ZnCo<sub>2</sub>O<sub>4</sub> + NCNT, and Co<sub>3</sub>O<sub>4</sub>/NCNT. However, the onset potential of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT composite is lower than that of commercial Pt/C (−0.05 V). It is of importance to mention that although ZnCo<sub>2</sub>O<sub>4</sub> or NCNT alone shows low ORR activity, the integration of ZnCo<sub>2</sub>O<sub>4</sub> onto NCNT leads to composite catalyst with greatly enhanced performance, suggesting the synergistic effect of two components in the composite. The superior catalytic performance for ZnCo<sub>2</sub>O<sub>4</sub>/NCNT composite could be attributed to that the strong coupling effects between ZnCo<sub>2</sub>O<sub>4</sub> and NCNT favor highly efficient charge transport in the composite for ORR catalysis [17]. The rotating disk electrode (RDE) measurements were applied to reveal the ORR kinetics of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT composite in O<sub>2</sub>-saturated 0.1 M KOH



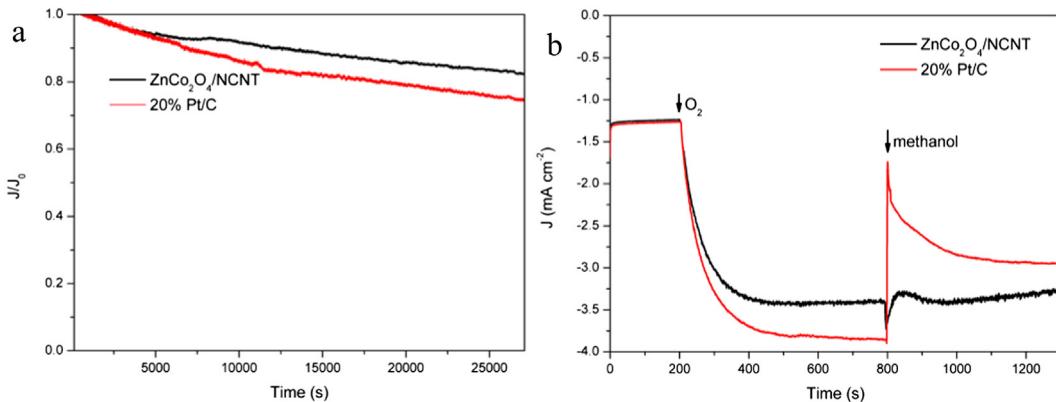
**Fig. 1.** (a) TEM image of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT (inset: HRTEM image of ZnCo<sub>2</sub>O<sub>4</sub> in the composite), (b) TEM image of ZnCo<sub>2</sub>O<sub>4</sub>, (c) XPS survey spectra of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT (inset: deconvoluted XPS N 1s spectrum), and (d) XRD patterns of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT and Co<sub>3</sub>O<sub>4</sub>/NCNT.

solution. As can be seen from Fig. 2c, increased rotation rate leads to an increase of limiting current density. The corresponding Koutecky–Levich plots at various potentials show good linearity and near parallelism (Fig. 2d), suggesting similar electron transfer

numbers for ORR at different potentials. This also indicates first-order reaction kinetics with respect to the concentration of dissolved O<sub>2</sub> [18]. The kinetic parameters can be analyzed on the basis of the Koutecky–Levich equations:



**Fig. 2.** (a) CV curves of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT, ZnCo<sub>2</sub>O<sub>4</sub>, NCNT, ZnCo<sub>2</sub>O<sub>4</sub> + NCNT, and Co<sub>3</sub>O<sub>4</sub>/NCNT on glassy carbon electrodes in O<sub>2</sub>-saturated (solid line) or N<sub>2</sub>-saturated (dash line) 0.1 M KOH solution with a sweep rate of 20 mV s<sup>-1</sup>. (b) LSVs of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT, ZnCo<sub>2</sub>O<sub>4</sub>, NCNT, ZnCo<sub>2</sub>O<sub>4</sub> + NCNT, Co<sub>3</sub>O<sub>4</sub>/NCNT, and Pt/C in O<sub>2</sub>-saturated 0.1 M KOH solution at a sweep rate of 5 mV s<sup>-1</sup> at 1600 rpm. (c) LSVs of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT in O<sub>2</sub>-saturated 0.1 M KOH solution at different rotation rates with a sweep rate of 5 mV s<sup>-1</sup>. (d) Corresponding Koutecky–Levich plots of ZnCo<sub>2</sub>O<sub>4</sub>/NCNT at a potential range of -0.4 V to -0.7 V.



**Fig. 3.** (a) Current–time chronoamperometric responses for ORR on  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  and Pt/C catalysts at  $-0.3$  V vs Ag/AgCl in  $\text{O}_2$ -saturated  $0.1$  M KOH solution at a rotation rate of  $1600$  rpm. (b) Current–time chronoamperometric responses of  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  and Pt/C at  $-0.3$  V vs Ag/AgCl in  $0.1$  M KOH solution at a rotation rate of  $1600$  rpm (the arrows indicate the introduction of  $\text{O}_2$  and methanol in sequence).

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{0.5}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFkC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

In which  $J$ ,  $J_K$ , and  $J_L$  correspond to the measured current density and the kinetic and diffusion-limiting current density, respectively,  $\omega$  is the angular velocity of the disk,  $n$  is transferred electron number,  $F$  is the Faraday constant,  $C_0$  is the bulk concentration of  $\text{O}_2$ ,  $D_0$  is the diffusion coefficient of oxygen,  $\nu$  is the kinematic viscosity of the electrolyte, and  $k$  is the electron-transfer rate constant. In this way,  $n$  for  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  composite was calculated to be  $3.7$ – $4.0$  throughout the tested potential range from  $-0.4$  to  $-0.7$  V, suggesting that  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  composite favors a four electron ORR pathway.

One main challenge for fuel cell applications is the durability of the catalysts. Fig. 3a shows the current–time chronoamperometric responses for ORR on  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  composite and Pt/C catalysts at  $-0.3$  V vs Ag/AgCl in  $\text{O}_2$ -saturated  $0.1$  M KOH solution at a rotation rate of  $1600$  rpm. Although the current densities of both catalysts initially decrease with time,  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  exhibits a relatively slow decay rate, maintaining  $82\%$  of their initial currents even after  $27500$  s, whereas the ORR current response for Pt/C decreases nearly  $30\%$ . These results indicate that  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  has superior durability over Pt/C catalyst, which can be ascribed to the strong coupling between  $\text{ZnCo}_2\text{O}_4$  and NCNT. Because the methanol tolerance ability is another important issue for ORR catalyst, the electrocatalytic sensitivity of  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  against methanol electrooxidation in ORR was also tested and compared with Pt/C catalyst, as shown in Fig. 3b. After adding methanol to the electrolyte (the resultant methanol concentration of  $3$  M),  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  composite retains a stable current response, suggesting a good methanol tolerance. In contrast, the current on Pt/C instantaneously decreases, indicating the occurrence of methanol oxidation reaction. Thus,  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  possesses much higher

selectivity toward ORR than Pt/C and is free from the methanol poisoning, promising for applications in fuel cells and other energy related devices.

#### 4. Conclusions

In summary,  $\text{ZnCo}_2\text{O}_4/\text{NCNT}$  composite has been successfully prepared by a solvothermal strategy for the first time. This composite exhibits superior ORR activity over  $\text{ZnCo}_2\text{O}_4$ , NCNT,  $\text{ZnCo}_2\text{O}_4 + \text{NCNT}$ , and  $\text{Co}_3\text{O}_4/\text{NCNT}$  catalysts. The catalyst also shows stronger tolerance to methanol and longer term stability than Pt/C catalyst. Such catalyst is promising as a highly efficient ORR catalyst in alkaline fuel cells and metal–air batteries [19].

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